

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.

(19) European Patent Office

(11)

**EP 1 069 142 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of Publication:

**Jan. 17, 2001 Patent Bulletin 2001/03**

(51) Int. Cl.<sup>7</sup>: **C08F 290/06, A61K 47/32**

**A61K 7/48, A01N 25/10**

(21) Application Number: **00114625.7**

(22) Application Date: **Jul. 07, 2000**

(84) Named Contracting States:  
**AT BE CH CY DE DK ES FI FR GB**  
**GR IE IT LI LU MC NL PT SE**  
Named Extension States  
**AL LT LV MK RO SI**

(30) Priority: **Jul. 15, 1999 DE 19933066**  
**Jun. 21, 2000 DE 10029462**

(71) Patent Holder: **Clariant GmbH**  
**65929 Frankfurt am Main (DE)**

(72) Inventor:

- **Morschhäuser, Roman, Dr.**  
**55122 Mainz (DE)**
- **Löffler, Matthias, Dr.**  
**65527 Niedernhausen (DE)**

(54) **Water-Soluble Polymers and Their Utilization in Cosmetics and Pharmaceuticals**

(57) Subject matter of the invention are water-soluble polymers, producible through the free-radical copolymerization of

A) one or more macromonomers, comprising an end group capable of polymerization, an hydrophilic part which is based on polyalkylene oxides, and a hydrophobic part which comprises hydrogen or a saturated or unsaturated, linear or branched, aliphatic, cycloaliphatic or aromatic (C<sub>1</sub>-C<sub>30</sub>) hydrocarbon residue, and

B) one or more olefinically unsaturated comonomers which comprise oxygen, nitrogen, sulfur, phosphorus, chlorine and or fluorine.

The polymers are suitable as thickeners, dispersing agents, emulsifiers, suspending agents, stabilizers and/or thickening agents<sup>1</sup> for aqueous formulations, emulsions and suspensions, in particular for cosmetics and pharmaceuticals.

<sup>1</sup> the German terms *Verdicker* and *Konsistenzgeber* are synonyms and are both translated as *thickener* or *thickening agent*. The authors of this patent are using both these terms, apparently as not really synonymous; the translation thus uses *Verdicker* = *thickener* and *Konsistenzgeber* = *thickening agent*, literally "consistency-giver".

## **Description**

[0001] The present invention concerns water-soluble polymers, prepared by copolymerization of macromonomers, and their utilization in cosmetics and pharmaceuticals.

[0002] Water-soluble polymers gained in the past years an increasingly growing significance in industry and science. In terms of the amount, polyelectrolytes occupy a very large portion of the annual total production of water-soluble polymers. They are utilized as flocculants in the paper production, the detergent industry, the textile processing, as protective colloids or in their cross-linked variations as thickener, so as to mention only a few areas of application.

[0003] Since their development in the 70ies, one can no longer picture the field of hygienics without thickeners, in particular those "superabsorbers" produced on the basis of the polyacrylic acid. Newer thickeners, like for instance the cross-linked polyacrylamido-propylene methylsulfonic acid (or their salts), are characterized by their clearly improved pH-stability and a better processibility.

[0004] For reasons of simplification of cosmetic formulations one increasingly seeks in the past years raw materials which combine a plurality of properties in one component of the formulation. Pure "thickeners" are replaced with new substances which have in their property profile, for example, also emulsifier properties and by that make unnecessary the addition to formulations of separate emulsifiers. The synthesis of the polymers described in the following offers the ideal instrument for this. The interesting combination of a polyelectrolyte (e.g., poly-AMPS) with non-polar molecule parts offers the possibility for a variation of the hydrophilic-hydrophobic balance of a polymer, as has been observed until now only in few cases in the synthetic polymer chemistry.

[0005] The temperature behavior of the polymers is an important property. At low temperatures, polymers show in general a high viscosity, and at high temperatures a low viscosity. But often desired are such polymers which above certain temperatures undergo thickening, but at low temperatures remain capable of being pumped into solution and processable.

[0006] EP-A-0 583 814 and EP-A-0 629 649 disclose polymers on the basis of acrylic acid as main chain and polyethylenes and/or polypropylene glycols as side-chains. These polymers show a thickening with increasing temperatures.

[0007] All attempts at production of such polymers on an industrial scale have until now remained unsuccessful. Moreover, the utilization of main chain polymers comprising acrylic acid were necessary for achieving the concept of thermothickening polymer solutions in water. One of the serious problems with this polymer class are precipitation phenomena based on instabilities with respect to divalent ions.

[0008] A new polymer class and a process for their production are now described in the present invention. With this process on the basis of a radical copolymerization, in particular the precipitation polymerization, it is possible without a great preparative expense to produce at industrial scale a multitude of new polymers with different thermal solubility characteristics.

[0009] It was surprisingly found that polymers which satisfy the requirements mentioned may also be produced by means of a macromonomer synthesis. This has as consequence the fact that the restriction to acrylic acid as one of the main chain monomers is rendered obsolete.

[0010] Subject matter of the invention are water-soluble polymers, producible through free radical copolymerization of

A) one or more macromonomers, comprising an end group capable of polymerization, an hydrophilic part which is based on polyalkylene oxides, and a hydrophobic part which comprises hydrogen or a saturated or unsaturated, linear or branched, aliphatic, cycloaliphatic or aromatic (C<sub>1</sub>-C<sub>30</sub>) hydrocarbon residue, and

B) one or more olefinically unsaturated comonomers which comprise oxygen, nitrogen, sulfur, phosphorus, chlorine and or fluorine.

[0011] In the case of the macromonomer A) one deals preferably with those with the Formula (1)



where  $R^1$  represents a vinyl, allyl, acrylic or methacrylic residue;  $R^2$  ( $C_2-C_4$ ) alkylene,  $x$  an integer number between 1 and 500;  $Y = O, S, PH$  or  $NH$ ; and  $R^3$  hydrogen or a saturated or unsaturated linear or branched aliphatic, cycloaliphatic or aromatic ( $C_{1-C_{30}}$ ) hydrocarbon.

[0012]  $R^1$  stands with particular preference for an acrylic or methacrylic residue.  $R^2$  stands with particular preference for an ethylene or propylene residue.  $x$  stands with particular preference for a number between 3 and 50, especially preferred for a number between 7 and 30. With  $R^3$  one preferably deals with aliphatic or cycloaliphatic hydrocarbons, which may be saturated or unsaturated.  $R^3$  stands with particular preference for a ( $C_6-C_{22}$ ) hydrocarbon residue, especially preferred for a ( $C_{12-C_{18}}$ ) hydrocarbon residue.

[0013] The production of the macromonomers is done in general via the reaction of reactive derivatives of the (meth)acrylic acid with compounds comprising hydroxyl groups, in particular alkoxylated alkyl residues. Also possible is the ring-opening addition to glycidyl (meth)acrylate.

[0014] Suitable as olefinic unsaturated comonomer B) are preferably olefinic unsaturated acids and their salts with monovalent and divalent counterions, especially preferred] styrene sulfonic acid, acrylamido-propylmethylene sulfonic acid (AMPS), vinyl sulfonic acid, vinyl phosphonic acid, allyl sulfonic acid, methallyl sulfonic acid, acrylic acid, (meth)acrylic acid, maleic acid or maleic anhydride and their salts; esters of the acrylic and the (meth)acrylic acid with aliphatic, aromatic or cycloaliphatic alcohols with a number of carbons of 1 to 22; esters of the acrylic and the (meth)acrylic acid with alkyl ethoxylates, open-chain and cyclic N-vinyl amides (N-vinyl lactames) with a ring size of 4 to 9 atoms, especially preferred N-vinyl formamide (NVF), N-vinyl methyl formamide, N-vinyl methyl acetamide (VIMA), N-vinyl acetamide, N-vinyl pyrrolidone (NVP) and N-vinyl caprolactam; amides of the acrylic and the methacrylic acid, especially preferred [are] acrylamide, N,N-dimethyl acrylamide, N,N-diethyl acrylamide, alkoxylated acrylamides and methacrylamides like, e.g., MAPTAC and APTAC; 2-vinylpyridine; 4-vinylpyridine; vinyl acetate; glycidyl (meth)acrylate; acrylonitrile; vinyl chloride; vinylidene chloride; tetrafluoroethylene and/or DADMAC.

**[0015]** Suitable as counterions for the salts of the olefinic unsaturated acids are preferably lithium, sodium, potassium, magnesium, calcium, ammonium, monoalkyl ammonium, dialkyl ammonium, trialkyl ammonium or tetraalkyl ammonium, where the alkyl substituents of the ammonium ions represent, independently of one another, (C<sub>1</sub>-C<sub>20</sub>) alkyl residues, which may be populated with 0 to 3 hydroxyalkyl groups, the alkyl chain length of which may vary in a range from C<sub>2</sub> to C<sub>10</sub>. Also suitable are mono- to tri-ethoxylated ammonium compounds of different degrees of ethoxylation. Sodium and ammonium are especially preferred as counterions. The degree of neutralization of the olefinically unsaturated acids is preferably between 70 and 100 mol%.

**[0016]** Especially preferred are water-soluble polymers, producible through the free-radical copolymerization of

A) one or more macromonomers, selected from the group of the esters of the (meth)acrylic acid with alkylethoxylates, which comprise 5 to 80 EO units and (C<sub>10</sub>-C<sub>22</sub>) alkyl residues, and

B) one or more olefinically unsaturated comonomers, selected from the group of acrylamidopropyl methylene sulfonic acid (AMPS), sodium and ammonium salts of the acrylamidopropyl methylene sulfonic acid (AMPS), acrylamide, N-vinyl formamide, N-vinyl methyl-acetamide and/or sodium methallyl sulfonate.

**[0017]** Particularly suitable hereby as macromonomers A) are esters of the (meth)acrylic acid with

- [C<sub>10</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 8 EO units (Genapol<sup>®</sup> C-080)
- C<sub>11</sub> oxo-alcohol polyglycol ether with 8 EO units (Genapol<sup>®</sup> UD-080)
- [C<sub>12</sub>-C<sub>14</sub>] fatty alcohol polyglycol ether with 7 EO units (Genapol<sup>®</sup> LA-070)
- [C<sub>12</sub>-C<sub>14</sub>] fatty alcohol polyglycol ether with 11 EO units (Genapol<sup>®</sup> LA-110)
- [C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 8 EO units (Genapol<sup>®</sup> T-080)
- [C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 15 EO units (Genapol<sup>®</sup> T-150)
- [C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 11 EO units (Genapol<sup>®</sup> T-110)
- [C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 20 EO units (Genapol<sup>®</sup> T-200)
- [C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 25 EO units (Genapol<sup>®</sup> T-250)
- [C<sub>18</sub>-C<sub>22</sub>] fatty alcohol polyglycol ether with 25 EO units

and/or iso-[C<sub>16</sub>-C<sub>18</sub>] fatty alcohol polyglycol ether with 2.5 EO units and suitable as olefinic unsaturated comonomers B) are in particular the sodium and ammonium salts of the acrylamidopropyl methylene sulfonic acid (AMPS). With the Genapol<sup>®</sup> types one deals with products of the Clariant Company.

**[0018]** The molar fractions of the macromonomers A) and the comonomers B) in the polymer may vary between 0.1 and 99.9 mol%.

In a preferred embodiment (highly hydrophobically modified polymers), the fraction of macromonomers A) is 50.1 to 99.9 mol%, preferably 70 to 95 mol%, especially preferred 80 to 90 mol%.

In a further preferred embodiment (non-highly hydrophobically modified polymers), the fraction of macromonomers A) is 0.1 to 50 mol%, preferably 5 to 25 mol%, especially preferred 10 to 20 mol%.

**[0019]** The monomer distribution of the macromonomers A) and comonomers B) in the polymers may be, for example, alternating, block-like (also multiblock) or else also random (also gradient).

The polymers have in general a number average molecular weight of 1000 to 20,000,000 g/mol, preferably 20,000 to 5,000,000, especially preferred 100,000 to 1,500,000 g/mol.

**[0020]** In a preferred embodiment, the polymers according to the invention are crosslinked, i.e., they comprise at least one cross-linking agent with at least two double bonds, which is polymerized into the polymer. Suitable cross-linking agents are in particular methylene bis-acrylamide and methylene methacrylamide, esters of unsaturated monocarboxylic or polycarboxylic acids with polyols, e.g., diacrylates or triacrylates like, e.g., butane diol and ethylene glycol diacrylate or methacrylate, and trimethylol propane triacrylate, allyl compounds like, e.g., allyl(meth)acrylate, triallyl cyanurate, diallyl maleate, polyallyl ester, tetraallyl oxyethane, triallyl amine, tetraallyl ethylene diamine, allyl esters of the phosphoric acid and/or derivatives of the vinyl phosphonic acid.

**[0021]** A preferred embodiment of the invention is constituted by such polymers which consist of a water-soluble polymer backbone and macromonomers A) with heat-sensitive side chains, which in water have an LCST behavior and the aqueous solution of

which has a viscosity which above a certain threshold temperature increases or remains approximately constant with the temperature increasing.

[0022] A further preferred embodiment of the invention is constituted by such polymers, the aqueous solution of which has a viscosity which below a first threshold temperature is low, above this first line increases to a maximum with the increasing temperature, and decreases again with temperature above a threshold temperature. It is thereby preferred for the viscosity of the polymer solution below the first threshold temperature to lie at 5 to 50%, in particular 10 to 30% of the maximum viscosity at the second threshold temperature.

[0023] Also representing a preferred embodiment are polymers, the aqueous solution of which has already at room temperature a high viscosity and which exhibit no thermoassociating behavior. The viscosities of the 1% aqueous solution are preferably 20,000 mPas to 100,000 mPas, in particular 60,000 mPas to 70,000 mPas.

Such polymers exhibit already at room temperature a high thickening performance, good emulsification properties and good dispersion properties in aqueous, aqueous -alcoholic and aqueous-surfactant solutions or in emulsions. Moreover, formulations comprising such polymers exhibit a good transparency and a high electrolyte stability.

[0024] The polymers according to the invention are produced by free -radical copolymerization like, e.g., precipitation polymerization, emulsion polymerization, solution polymerization or suspension polymerization. Suited with preference is the precipitation polymerization, most preferred the precipitation in tert. butanol.

[0025] Through precipitation polymerization in tert. butanol one can achieve a particle distribution of the polymers which is particularly favorable for the utilization of the polymers. The size distribution of the polymer particles can be determined, e.g., through laser diffraction or screen analysis. Representative for a suitable size distribution is the following grain size distribution, as determined by screen analysis for an AMPS copolymer: 60.2% smaller [than] 423 micrometers, 52.0% smaller [than] 212 micrometers, 26.6% smaller [than] 106 micrometers, 2.6% smaller [than] 45 micrometers and 26.6% larger [than] 850 micrometers.

[0026] The polymerization may be performed in the temperature range between 0 and 150°C, preferably between 10 and 100°C, at normal pressure as well as at elevated or

lowered pressure. The polymerization may also be performed, as usual, under protective atmosphere, preferably under nitrogen.

[0027] In order to initiate the polymerization one may use high-energy electromagnetic rays or the usual chemical polymerization initiators, e.g., organic peroxides, like benzoyl peroxide, tert. butyl hydroperoxide, methyl ethyl ketone peroxide, cumene hydroperoxide, azo compounds like, e.g., azo-bis-isobutyronitrile, azo-bis-dimethyl valeronitrile, as well as inorganic peroxy compounds like, e.g.,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$  or  $\text{H}_2\text{O}_2$ , possibly in combination with reducing agents like, e.g., sodium hydrogen sulfite and iron (II) sulfate, or redox systems which comprise as the reducing component an aliphatic or aromatic sulfonic acid like, e.g., benzene sulfonic acid, toluene sulfonic acid or derivatives of these acids like, e.g., Mannich adducts of sulfonic acid, aldehydes and amino-compounds.

[0028] The polymers according to the invention are suitable as thickeners and dispersing agents for aqueous formulations, aqueous-alcoholic and aqueous-surfactant formulations and emulsifiers, suspending agents with thickening effect and thickening agents for emulsions and suspensions. One may thereby use also mixtures of the polymers. The polymers are especially suitable for the utilization in cosmetics and pharmaceuticals.

Important is thereby that the polymers can be used without the combined utilization of an additional co-emulsifier and/or without the combined utilization of an additional thickening agents. The combined utilization of co-emulsifiers and thickening agents is for that reason not mandatory, but possible.

[0029] Subject matter of the invention are thus also aqueous formulations, aqueous-alcoholic formulations, aqueous-surfactant formulations, emulsions and suspensions, comprising the polymers according to the invention. With the formulations, emulsions and suspensions one deals preferably with cosmetics and pharmaceuticals like, e.g., shampoos, shower soap<sup>2</sup>, shower gels, bubble baths, gels, lotions, creams and ointments.

---

<sup>2</sup> The German terms *Duschbad* and *Duschgel* are usually both translated as *shower gel*; in order to be able to distinguish between the two terms used by the authors, the translation sets *Duschbad* = *shower soap* (literal translation *shower bath*) and *Duschgel* = *shower gel*

[0030] The formulations, emulsions and suspensions according to the invention have in relation to the finished formulation preferably 0.05 to 10 wt.%, particularly preferred 0.1 to 5 wt.%, especially preferred 0.5 to 3 wt.%, of polymers according to the invention.

[0031] The polymers according to the invention can be used as thickeners for preparations on an aqueous or aqueous-alcoholic basis, for example, hair [styling] gels. The polymers according to the invention are furthermore suitable for aqueous-surfactant formulations, for example shampoos, shower soaps, shower gels, bubble baths and the like. The thickening effect of the polymers according to the invention in aqueous-surfactant preparations is increased through an association of the polymer side chains and the surfactants and can be controlled through the selection of the side chains of the polymers and through the selection of the surfactants. The suspending or dispersing and stabilizing effect of the polymers according to the invention in aqueous-surfactant preparations is caused through the association of the polymer side chains and the fluid components insoluble in the aqueous-surfactant components, for example, silicone oils, or the insoluble components, for example, zinc pyrethions.

[0032] As additional auxiliary agents and additives, the preparations according to the invention may comprise all usual anionic, cationic, zwitterionic, non-ionic and amphoteric surfactants as well as further additives customary in cosmetics like, e.g., superfatting agents, stabilizers, biogenic agents, glycerin, preserving agents, pearlescent agent, dyestuff and fragrances, solvents, opacifiers, further thickening agents, and dispersing agents, furthermore protein derivatives like gelatins, collagen hydrolyzates, polypeptides on natural and synthetic basis, egg yolk, lecithin, lanolin and lanolin derivatives, fatty alcohols, silicones, deodorants, substances with keratolytic and keratoplastic effect, enzymes and carrier substances. One may further add anti-microbially acting agents to the preparations according to the invention.

[0033] The total amount of the surfactants used in the preparations according to the invention may be between 5 and 70 wt.%, preferably between 10 and 40 wt.%, especially preferred between 12 and 35 wt.% in relation to the finished preparation.

As anionic active detergent substances one should mention: (C<sub>10</sub>-C<sub>20</sub>)-alkyl and alkylene carboxylates, alkyl ether carboxylates, fatty alkyl sulfates, fatty alkyl ether sulfates, alkyl amide sulfates and sulfonates, fatty alkyl amido-polyglycol ether sulfate, alkane sulfonate

and hydroxyalkane sulfonates, olefin sulfonates, acyl esters of isetonates, esters of  $\alpha$ -sulfofatty acid, alkylbenzene sulfonate, alkylphenol glycol ether-sulfonate, sulfosuccinate, half-ester and diester of the sulfo-succinic acid, fatty alkyl ether phosphate, protein-fatty acid condensation products, alkyl monoglyceride sulfates and sulfonates, alkyl glyceride ether sulfonates, fatty acid methyl tauride, fatty acid sarcosinate, sulfo-ricinoleates, acyl glutamates. These compounds and their mixtures are used in the form of their water-soluble or in water dispersed salts, for example, the sodium, potassium, magnesium, ammonium, mono-, di- and triethanol ammonium salts as well as analogous alkyl ammonium salts.

**[0034]** The weight fraction of the anionic surfactants in the preparations according to the invention lies preferably in the range from 7 to 30 wt.%, especially preferred 10 to 25 wt.%, most specially preferred 12 to 22 wt.%.

**[0035]** Suitable cationic surfactants are, for example, quaternary ammonium salts like di-(C<sub>10</sub>-C<sub>24</sub>)-alkyl-dimethyl ammonium chloride or bromide, preferably di-(C<sub>12</sub>-C<sub>18</sub>)-alkyl-dimethyl ammonium chloride or bromide; (C<sub>10</sub>-C<sub>24</sub>)-alkyl-trimethyl ammonium chloride or bromide, preferably cetyl trimethyl ammonium chloride or bromide, and (C<sub>20</sub>-C<sub>22</sub>)-alkyl-trimethyl ammonium chloride or bromide; (C<sub>10</sub>-C<sub>24</sub>)-alkyl-dimethyl benzyl ammonium chloride or bromide, preferably (C<sub>12</sub>-C<sub>18</sub>)-alkyl-dimethyl benzyl ammonium chloride; N-(C<sub>10</sub>-C<sub>18</sub>)-alkyl-isoquinoline chloride, bromide or monoalkyl sulfate; N-(C<sub>12</sub>-C<sub>16</sub>)-alkyl-pyridinium chloride or methyl pyridinium chloride; N-(C<sub>12</sub>-C<sub>18</sub>)-alkyl-N-methyl-morpholinium chloride, bromide or monoalkyl sulfate; N-(C<sub>12</sub>-C<sub>18</sub>)-alkyl-N-ethyl-morpholinium chloride, bromide or monoalkyl sulfate; (C<sub>16</sub>-C<sub>18</sub>)-alkyl-pentaoxethyl-ammonium chloride; diisobutyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride; salts of the N,N-diethyl aminoethyl stearyl amide and oleyl amide with hydrochloric acid, acetic acid, lactic acid, citric acid, phosphoric acid; N-acyl-aminoethyl-N,N-diethyl-N-methyl ammonium chloride, bromide or monoalkyl sulfate and acyl aminoethyl-N,N-diethyl-N-benzyl-ammonium chloride, bromide or monoalkyl sulfate, where acyl stands preferably for stearyl or oleyl.

**[0036]** The weight fraction of the cationic surfactants in the preparations according to the invention lies with preference in the range from 1 to 10 wt.%, especially preferred between 2 to 7 wt.%, most specially preferred between 3 to 5 wt.%.

**[0037]** As non-ionic surfactants which may be used as active detergent substances one may take into consideration, for example: fatty alcohol ethoxylates (alkyl polyethylene glycols); alkylphenol polyethylene glycols; alkyl mer captane polyethylene glycols; fatty amine ethoxylates (alkylamino polyethylene glycols); fatty ethoxylates (acyl polyethylene glycols); polypropylene glycol ethoxylates (Pluronic<sup>®</sup>); fatty acid alkylol amides (fatty acid amide polyethylene glycols); N-alkyl-, N-alkoxy-polyhydroxy-fatty acid amides, sucrose ester, sorbite ester and polyglycol ether.

**[0038]** The weight fraction of the non-ionic surfactants in the preparations according to the invention lies preferably in the range from 1 to 20 wt.%, particularly preferred 2 to 10 wt.%, most specially preferred 3 to 7 wt.%.

**[0039]** Preferred amphi-surfactants are: N-(C<sub>12</sub>-C<sub>18</sub>)-alkyl-β-aminopropionates and N-(C<sub>12</sub>-C<sub>18</sub>)-alkyl-β-iminodipropionates as alkali- and mono-, di- and trialkyl-ammonium salts; N-acylaminoalkyl-N,N-dimethyl-acetobetaine, preferably N-(C<sub>8</sub>-C<sub>18</sub>)-acyl-aminopropyl-N,N-dimethyl acetobetaine; (C<sub>12</sub>-C<sub>18</sub>)-alkyl-dimethyl-sulfopropyl-betaine; amphi-surfactants on the basis [of] imidazoline (trade name: Miranol<sup>®</sup>, Steinapon<sup>®</sup>), preferably the sodium salt of the 1-(β-carboxy-methyloxy-ethyl)-1-(carboxymethyl)-2-lauryl-imidazolinium; aminoxides, e.g., (C<sub>12</sub>-C<sub>18</sub>)-alkyl-dimethyl aminoxide, fatty acid amidoalkyl-dimethyl-aminoxide.

**[0040]** The weight fraction of the amphoteric surfactants in the preparations according to the invention lies preferably in the range from 0.5 to 20 wt.%, particularly preferred 1 to 10 wt.%.

**[0041]** In the preparations according to the invention one may further use foam-enhancing co-surfactants from the group [of] alkyl betaines, alkyl amido betaines, aminopropionates, amino-glycinates, imidazolinium betaines and sulfobetaines, aminoxides and fatty acid alkanol amides or polyhydroxy amides.

**[0042]** Surfactants preferred in the preparations according to the invention are lauryl sulfate, laureth sulfate, cocamido-propyl-betaine sodium cocoyl glutamate, di-sodium-laureth-sulfosuccinate and coco fatty-diethanol-amide.

The formulations according to the invention may additionally comprise further additives common in cosmetics like superfatting agents, stabilizers, biogenic active substances, glycerin, preserving agents, pearlescent agents, dyestuff and fragrances, solvents,

opacifiers, thickening agents, and dispersing agents, furthermore protein derivatives like gelatins, collagen hydrolyzates, polypeptides on natural and synthetic bases, egg yolk, lecithin, lanolin and lanolin derivatives, fatty alcohols, silicones, deodorants, substances with keratolytic and keratoplastic effect, enzymes and carrier substances. One may further add anti-microbially acting agents to the preparations according to the invention.

Substances like, for example, polyethoxylated lanolin derivatives, lecithin derivatives, esters of polyol-fatty acids, monoglycerides and alkanol amides of fatty acids, where the latter serve simultaneously as foam stabilizers. Glycerides are typical examples of fats, as waxes one may consider, among other things, bees wax, paraffin wax or microwaxes, possibly in combination with hydrophilic waxes, e.g., cetyl stearyl alcohol.

**[0043]** Metal salts of fatty acids like, e.g., magnesium, aluminum and/or zinc stearate may be used as stabilizers.

As biogenic agents one may understand, for example, plant extracts and vitamin complexes.

As pearlescent agents one may consider, for example, esters of glycol di stearic acid, like ethylene glycol distearate, but also fatty acid monoglycol esters.

As dyes one may use substances which are suitable and approved for cosmetic purposes.

**[0044]** Suitable as further thickening agents are sodium chloride, potassium chloride, sodium sulfate, fatty acid alkylol amides, cellulose derivatives, for example, hydroxyethyl cellulose, guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, as well as natural gummen, carboxyl vinyl polymers, for example, Carbopol 934, 940, 941, 956, 980, 981, 1342, 1382, ethylene glycol esters of fatty acids with 14 to 22, especially preferred 16 to 22 carbon atoms, in particular mono- and diethylene glycol stearate. Also preferred are stearin monoethanol amide, stearin diethanol amide, stearin isopropanol amide, stearin monoethanol amide stearate, stearyl stearate, cetyl palmitate, glyceryl stearate, stearamide diethanol amide distearate, stearamide monoethanol amide stearate, N,N-dihydrocarbyl-(C<sub>12</sub>-C<sub>22</sub>), in particular (C<sub>15</sub>-C<sub>18</sub>)-amidobenzoic acid and their soluble salts, N,N-di(C<sub>16</sub>-C<sub>18</sub>)-aminobenzoic acid and its derivatives. In relation to the finished preparation, the dispersing agents are used in concentrations of preferably 0.5 to 10 wt.%, especially preferred 0.5 to 10 wt.%, most specially preferred from 0.5 to 5 wt.%, preferred in particular from 1 to 4 wt.%.

The desired viscosity of the preparations can be adjusted through the addition of water and/or organic solvents or through the addition of a combination of organic solvents and thickening agents.

As organic solvents one may in principle consider all mono - or polyhydric alcohols. Preferred are alcohols with 1 to 4 carbon atoms, like ethanol, propanol, isopropanol, n-butanol, i-butanol, t-butanol, glycerin, and mixtures of the alcohols mentioned. Further preferred alcohols are polyethylene glycols with a relative molecular weight below 2000. Particularly preferred is a utilization of polyethylene glycol with a relative molecular weight between 200 and 600 and in amounts of up to 45 wt.% and of polyethylene glycol with a relative molecular weight between 400 and 600 in amounts of 5 to 25 wt.%. Triacetin (glycerin triacetate) and 1-methoxy-2-propanol are further suitable solvents.

[0045] Vegetable oils, natural and hydrogenated oils, waxes, fats, water, alcohols, polyols, glycerol, glyceride, fluid paraffins, sterol, polyethylene glycols, cellulose and cellulose derivatives may be considered as carrier materials.

[0046] As fungicides one may use ketoc onazole, oxiconazole, bifonazole, butoconazole, cloconazole, clotrimazole, econazole, enilconazole, fenticonazole, isoconazole, miconazole, sulconazole, tioconazole, fluconazole, itraconazole, terconazole, naftifine and terbinafine.

[0047] Silicones, polysiloxanes, polyalkylarylailoxanes, polyether-siloxane copolymers, as described in US 5 104 645 and the documents cited herein, further improve the nourishing effect of the preparations according to the invention. The preparations according to the invention can be mixed with conventional ceramides, pseudo-ceramides, fatty acid-N-alkyl-polyhydroxyalkyl-amide, cholesterol, cholesterol fatty acid esters, fatty acids, triglycerides, cerebrosides, phospholipids and similar substances.

[0048] The polymers according to the invention may be used in emulsions as emulsifiers, stabilizers and/or thickening agents. Cross-linked polymers are particularly suitable for that. In the case of the emulsions one may deal with water-in-oil emulsions as well as with oil-in-water emulsions.

The emulsifying, stabilizing and/or thickening effect of the polymers in emulsion according to the invention is caused or heightened through an association of the polymer

side chains with one another, as well as through an interaction of the polymer side chains with the hydrophobic oil components.

**[0049]** The non-aqueous fraction of the emulsions, which is largely composed of the emulsifier, the thickener and the oil body, lies usually at 5 to 95%, preferably at 15 to 75 wt%. From that follows that the emulsions may comprise 5 to 95 wt.% and preferably 25 to 85 wt.% of water, as a function of whether it is intended to produce lotions with a relatively low [viscosity] or creams and ointments with a high viscosity.

**[0050]** The emulsions may be used as skin care preparations like, for example, day cream, night cream, [protective] care creams, nourishing cream, body lotions, ointments and the like, and comprised as further auxiliary agent and additives, oil bodies, co-emulsifiers, superfatting agents, fats, waxes, stabilizers, biogenic active substances, glycerin, preservatives, dyestuff and fragrances.

**[0051]** As oil body one may take into consideration, for example, Guerbet alcohols on the basis of fatty alcohols with 6 to 18, preferably 8 to 10 carbon atoms, esters of linear ( $C_6-C_{13}$ ) fatty acids with linear ( $C_6-C_{20}$ ) fatty alcohols, esters of branched ( $C_6-C_{13}$ ) carboxylic acids with linear ( $C_6-C_{20}$ ) fatty alcohols, esters of linear ( $C_6-C_{18}$ ) fatty acids with branched alcohols, in particular 2-ethyl hexanol, esters of linear and/or branched fatty acids with polyhydric alcohols (like, e.g., dimer-diol or trimer-diol) and/or Guerbet alcohols, triglycerides on the basis [of] ( $C_6-C_{10}$ ) fatty acids, vegetable oils, branched primary alcohols, substituted cyclohexanes, Guerbet carbonates, dialkyl ethers and/or aliphatic or aromatic hydrocarbons. The fraction of oil bodies within the non-aqueous fraction of the emulsions can make up 5 to 95 and preferably 15 to 75 wt.%.

**[0052]** As non-ionogenic co-emulsifiers one may consider, among other things, addition products of 0 to 30 mol ethylene oxide and/or 0 to 5 mol propylene oxide to linear fatty alcohols with 8 to 22 C-atoms, to fatty acids with 12 to 22 C-atoms, to alkyl phenols with 8 to 15 C-atoms in the alkyl group, and sorbitan or sorbitol esters; ( $C_{12}-C_{18}$ )-fatty acid mono- or diesters of addition products of 0 to 30 mol ethylene oxide to glycerin; glycerin mono- and diesters and sorbitan mono- and diester of saturated and unsaturated fatty acids with 6 to 22 carbon atoms and possibly their ethylene oxide addition products; addition products of 15 to 60 mol ethylene oxide to castor oil and/or hardened castor oil; polyol esters and in particular polyglycine esters like, e.g.,

polyglycerin polyricinoleate and polyglycerin poly-12-hydroxystearate. Also suitable are mixtures of compounds from several of these classes of substances.

[0053] Suitable as ionogenic co-emulsifiers are, e.g., anionic emulsifiers like mono-, di- or tri-phosphates, but also cationic emulsifiers like mono-, di- and tri-alkyl-quats and their polymeric derivatives.

A multitude of different systems are indicated in literature for adjusting the rheological properties of aqueous or solvent-containing emulsions or suspensions. Known are, for example, cellulose ethers and other cellulose derivatives (e.g., carboxymethyl cellulose, hydroxyethyl cellulose), gelatin, starch and starch derivatives, sodium alginates, fatty acid polyethylene glycol, agar-agar, tragacanth or dextrans. Various materials are utilized as synthetic polymers, e.g., polyvinyl alcohols, polyacrylamides, polyvinyl amides, polysulfonic acid, polyacrylic acid, polyacrylate, polyvinyl pyrrolidone, polyvinyl methyl ether, polyethylene oxide, copolymers of maleic anhydride and vinyl methyl ether, as well as various mixtures and copolymers of the above mentioned compounds, including their various salts and esters. These polymers may optionally be crosslinked or not crosslinked. The preparation of the emulsions may take place in known ways, i.e., for example, through hot, hot/cold or PIT emulsification.

[0054] The polymers according to the invention can also be used for the formulation of crop protection chemicals. In this area of application one came in the past years to a rethinking in the development of new formulations of active substances. It was not the research for new active substances which was at the forefront, but the search for auxiliary reagents for the enhancement of the effect of known active substances at the surface of plants. The addition of so-called adjuvants enables the reduction of the amounts of active substances used while maintaining the efficiency of the overall formulation if compared to the formulations free of adjuvants. On one hand, non-polar modified water-soluble polyelectrolytes make possible an increase in the viscosity of the active substance solution at hand, which leads to a slower "pearling" from the surface of the leaf and by that to a prolonged contact time on the leaf, and on the other hand, the non-polar side [chain] residues cause an increased adsorption to the likewise non-polar surfaces of the leaves.

**[0055]** The following examples and applications shall explain the invention more closely, without restricting it, however.

#### Examples and Applications

##### 1) Preparation of the Macromonomers

###### a) Method 1: Glycidyl methacrylate

**[0056]** In a 1 liter three-necked flask with stirrer, internal thermometer, and reflux condenser one sets up 600 g of Genapol T-250 and reacts it with 75 g glycidyl methacrylate. The reaction mixture is then heated for 2 hours at 100°C and the excess glycidyl methacrylate is distilled off in the vacuum. The macromonomer formed can be used in the polymerization without further cleaning.

###### b) Method 2: Free meth/acrylic acid

**[0057]** In a 1 liter three-necked flask with stirrer, inner thermometer, and reflux condenser one sets up 500 g of Genapol UD-070 and reacts it with 100 g meth/acrylic acid and p-toluene sulfonic acid as catalyst. The reaction mixture is then boiled for 2 hours under reflux and the excess ester and the reaction water are distilled off in the vacuum. The macromonomer formed can be used in the polymerization without further cleaning.

###### c) Method 3: Halogen derivatives of meth/acrylic acid

**[0058]** In a 1 liter three-necked flask with stirrer, inner thermometer, and reflux condenser one sets up 500 g of Genapol UD-070 with a primary amino end group and reacts it with 110 g meth/acrylic acid and 50 g sodium carbonate. The reaction mixture is then boiled for 2 hours under reflux. The development of CO<sub>2</sub> coming to an end indicates the end of the modification reaction. The excess acid chloride is distilled off in the vacuum. The macromonomer formed, having a meth/acrylamide group, can be used in the polymerization without further cleaning.

##### 2) Polymerization

General polymerization specification for the preparation of side chain polymers according to the invention following the precipitation procedure in t -butanol

[0060] In a 2-liter quick-fit flask with reflux condenser, gas inlet, inner thermometer and stirrer one sets up 500 ml t-butanol and reacted with the pre -calculated amount of AMPS. One then neutralizes through the introduction of  $\text{NH}_3$  and the LCST side chains, as produced under 1) (various different species also possible), are added to the reaction mixture. Should one need further comonomers, then these may be added to the reaction mixture following the neutralization. Following inertization with  $\text{N}_2$  or argon, AIBN is added as initiator at an internal temperature of 60°C and the polymerization reaction is initiated. The finished polymer precipitates after a few minutes. The mixture is heated for two hours under reflux and the polymer is then freed of the solvent via a vacuum filter and dried in the vacuum. This specification is generally usable in all polymer reactions described in the following.

#### Side Chain Polymers With Thickener Properties

Example 1: Reaction according to the general polymerization specification

[0061]

Reactant	Amount (g)
Macromonomer	20
Method 1 - type Genapol® T-250	
$\text{NH}_3$ neutralized AMPS	100
t-butanol	300
AIBN (initiator)	1

Example 2: Reaction according to the general polymerization specification

[0062]

Reactant	Amount (g)
Macromonomer	30
Method 3 - type Genapol® UD-800	
$\text{NH}_3$ neutralized AMPS	90
t-butanol	300
AIBN (initiator)	1

Example 3: Reaction according to the general polymerization specification

[0063]

Reactant	Amount (g)
Macromonomer	30
Method 3 - type Genapol® T-250	
NH <sub>3</sub> neutralized AMPS	90
methylene-bis-acrylamide (crosslinking agent)	
t-butanol	300
AIBN (initiator)	
	1

Example 4: Reaction according to the general polymerization specification

[0064]

Reactant	Amount (g)
Macromonomer	20
Method 1 - type Genapol® L-070	
Na neutralized AMPS	75
Acrylamide	50
AIBN (initiator)	1

Example 5: Reaction according to the general polymerization specification

[0065]

Reactant	Amount (g)
Macromonomer	15
Method 4 - type Genapol® UD-080	
Macromonomer method 1 - type Genapol® T-250	15
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
AIBN (initiator)	1

Example 6: Reaction according to the general polymerization specification

[0066]

Reactant	Amount (g)
Macromonomer	20
Method 1 - type Genapol <sup>®</sup> LA-110	
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
AIBN (initiator)	1

Example 7: Reaction according to the general polymerization specification

[0067]

Reactant	Amount (g)
Macromonomer	20
Method 1 - type Genapol <sup>®</sup> T-080	
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
AIBN (initiator)	1

Example 8: Reaction according to the general polymerization specification

[0068]

Reactant	Amount (g)
Macromonomer	25
Method 1 - type Genapol <sup>®</sup> T-150	
NH <sub>3</sub> neutralized AMPS	100
AM	10
t-butanol	350
AIBN (initiator)	1

Example 9: Reaction according to the general polymerization specification

[0069]

	9.1	9.2	9.3
Reactant	Amount (g)	Amount (g)	Amount (g)
Macromonomer	10	20	10
Method 1 - type Genapol <sup>®</sup> LA-110			
Macromonomer	12.5	12.5	25
Method 1 - type Genapol <sup>®</sup> T-150			
NH <sub>3</sub> neutralized AMPS	100	100	100
AM	10	10	10
t-butanol	350	350	350
AIBN (initiator)	1	1	1

Example 10: Polymer mixture

[0070]

	10.2	10.2	10.3
Polymer	Amount (g)	Amount (g)	Amount (g)
Example 1	10	20	10
Example 3	10	10	20

Example 11: Reaction according to the general polymerization specification, but with a starting temperature of 45°C

[0071]

Reactant	Amount (g)
Macromonomer	25
Method 1 - type (C <sub>18</sub> -C <sub>22</sub> ) fatty alcohol polyglycol ether with 25 EO units	
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
Azo-bis-dimethyl valeronitrile (initiator)	1

Example 12: Reaction according to the general polymerization specification, but with a starting temperature of 45°C

[0072]

Reactant	Amount (g)
Macromonomer	20
Method 1 - type Genapol <sup>®</sup> UD-080	
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
Azo-bis-dimethyl valeronitrile (initiator)	1

Example 13: Reaction according to the general polymerization specification

[0073]

Reactant	Amount (g)
Macromonomer	15
Method 1 - type Genapol <sup>®</sup> T-200	
NH <sub>3</sub> neutralized AMPS	100
t-butanol	300
AIBN (initiator)	1

Example 14: Reaction according to the general polymerization specification

[0074]

Reactant	Amount (g)
Genapol <sup>®</sup> T-250 methacrylate	97
NH <sub>3</sub> neutralized AMPS	3
t-butanol	300
TMPTA	1.8
Dilauroyl peroxide (initiator)	1

Example 15: Reaction according to the general polymerization specification

[0075]

Reactant	Amount (g)
MPEG 750-methacrylate	80
NH <sub>3</sub> neutralized AMPS	20
t-butanol	300
TMPTA	1.8
Dilauroyl peroxide (initiator)	1

Viscosity 1.0% (dist. H<sub>2</sub>O) 55,000 mPas (Brookfield Spindle 7)

Viscosity 10.5% (dist. H<sub>2</sub>O) 19,000 mPas (Brookfield Spindle 7)

Example 16: Reaction according to the general polymerization specification

[0076]

Reactant	Amount (g)
Genapol® T-250 methacrylate	97
NH <sub>3</sub> neutralized AMPS	3
t-butanol	300
Dilauroyl peroxide (initiator)	1

Example 17: Reaction according to the general polymerization specification

[0077]

Reactant	Amount (g)
MPEG-750-methacrylate	20
NH <sub>3</sub> neutralized AMPS	80
t-butanol	300
ABAH (initiator)	1

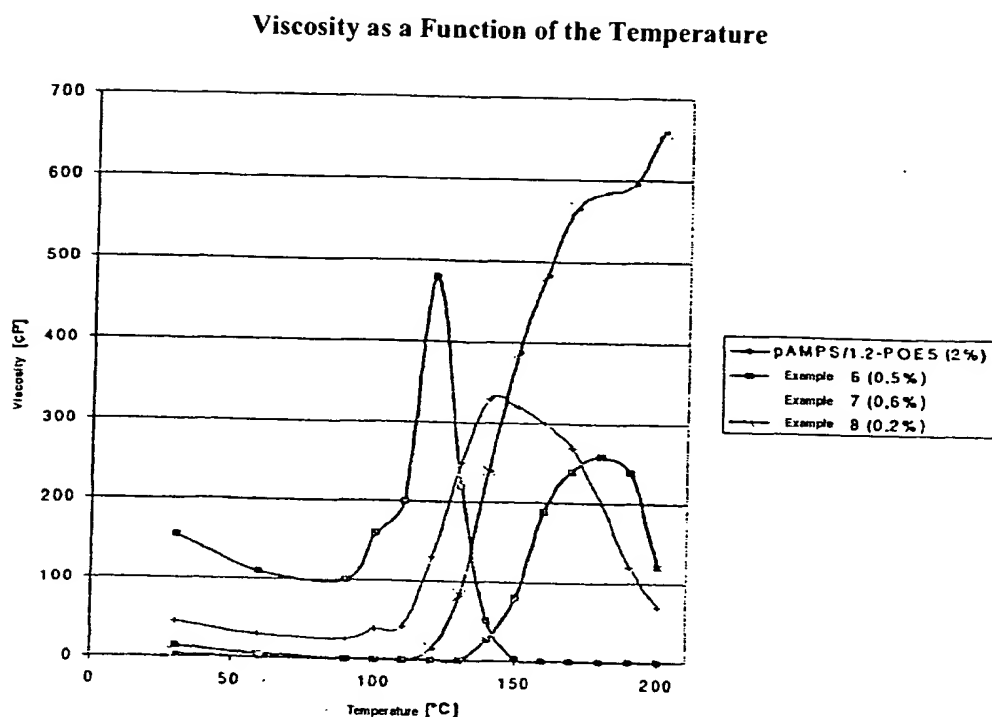
Viscosity 1.0% (dist. H<sub>2</sub>O) 1,500 mPas (Brookfield Spindle 5)

Viscosity 10.5% (dist. H<sub>2</sub>O) 19,000 mPas (Brookfield Spindle 5)

Comparison Example 1:

[0078] The comparison example 1 shows that the temperature at which the viscosification commences and the intensity of the effect can be influenced (Figure 1). The polymers used are based on the Examples 6, 7 and 8. Moreover, a polymer is further reproduced from EP-B-0 583 814. One deals thereby with pAMP S/1,2-POE5 from Example 1.3. Figure 1 shows the viscosity of the polymers in aqueous solution. In Figure 1 one can recognize that the maxima of the viscosification can be found at different temperatures: at 120°C for Example 6, at 140°C for Example 7 and at above 200 ° for Example 8. pAMPS/1,2-POE5 has its temperature maximum at 200°C. Moreover, the concentrations used are clearly lower than for pAMPS/1,2 -POE5 (Figure 1).

Figure 1



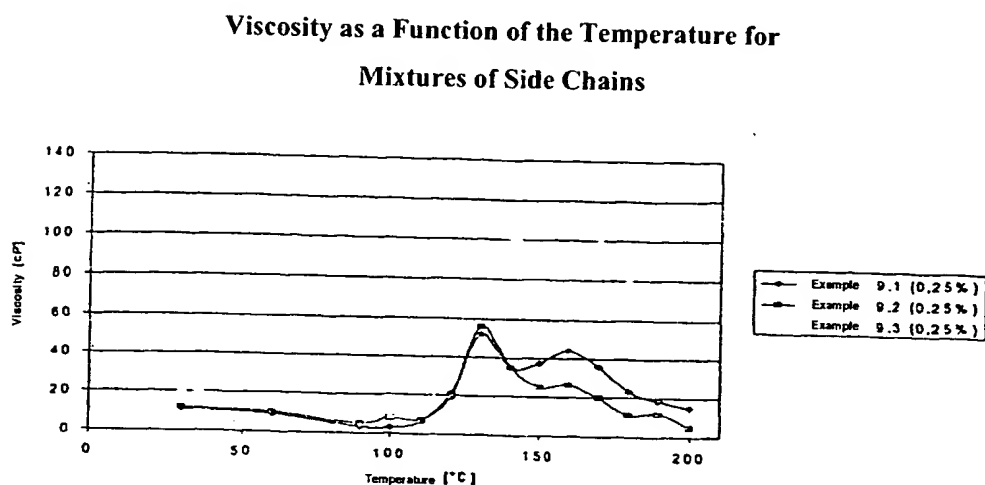
[0079] One further clearly recognizes that based on the hydrophobic interactions of the alkyl residues of the side chains, the polymers according to the invention have already at room temperature an intrinsic viscosity. pAMPS/1,2 -POE5 does not develop such an intrinsic viscosity. The polymers according to the invention are further characterized in that the breadth of the thermoassociating effects are controllable.

[0080] The influence of various side chains in a polymer (Example 18) and the influence of mixtures of various polymers (Example 19) are explained in the two examples that follow.

Example 18:

[0081] This example shows the development of the viscosity at various temperatures for the polymers from Example 9. One uses various side chains in one polymer (Figure 2).

Figure 2

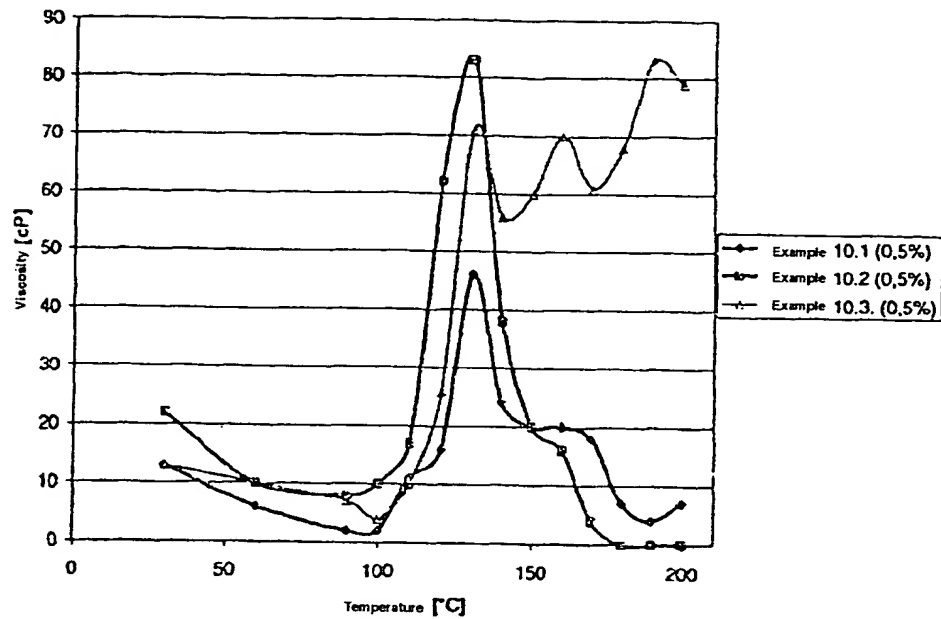


Example 19:

[0082] In Figure 3 it is shown how the viscosity behavior changes as a function of the temperature. The Examples 10,1 through 10.3 are different ratios of mixing of the polymers from Example 6 and Example 7. The breadth and intensity of the thermoassociating effect can be adjusted via the mixing ratio.

Figure 3

### Viscosity Behavior of Polymer Mixtures



### Examples of Oil Emulsions

[0083] The test emulsions are stored at 40°C, 45°C and 50°C over a time period of 90 days, 3 different oil mixtures are used each time. The oil mixtures are composed as follows:

Mixture I:		Mixture II:	
Paraffin oil low visc.	50%	Cetiol V	25%
Isopropyl palmitate	30%	Squalane	25%
Soybean oil	20%	Myritol 318	25%
		Isopropyl palmitate	25%
Mixture II:			
Soybean oil	50%		
Almond oil	20%		
Avocado oil	20%		
Jojoba oil	10%		

**Evaluation Key:**

**[0084]**

- 0 = no emulsifier effect
- 1 = separated into 2 or 3 phases
- 3 = creaming + oil or water + creaming, homogeneous emulsion in between
- 4 = water separation, no creaming, no oil separation
- 5 = oil separation, no creaming, no water separation
- 6 = creaming
- 7 = poorly recognizable creaming
- 8 = practically all right
- 9 = completely homogeneous emulsion

**Emulsification Index:**

**[0085]**

- 4.1 - 5.0 = very good
- 3.1 - 4.0 = good
- 2.1 - 3.0 = average
- 1.1 - 2.0 = poor
- 0 - 1.0 = very poor

Test emulsions with uncrosslinked polymers according to the invention.

[0086]

Composition	20	21	22	23	24	25	26	27	28	29	30	31
Polymer acc. to Ex. 2	-	-	-	1.0	-	-	1.0	-	-	0.5	-	-
Polymer acc. to Ex. 1	-	1.0	1.0	-	-	1.0	-	-	1.0	-	-	0.5
Polymer acc. to Ex. 6	1.0	-	-	-	1.0	-	-	1.0	-	-	0.5	-
Oil mixture I	19.0	19.0	-	-	-	-	-	-	-	-	-	-
Oil mixture II	-	-	19.0	-	-	-	-	-	-	-	-	-
Oil mixture III	-	-	-	19.0	19.0	19.0	27.0	27.0	27.0	27.0	27.0	27.0
Carbopol 980	0.3	0.3	0.3	0.3	0.3	0.3	-	-	-	-	-	-
Sodium hydroxide 10%	1.2	1.2	1.2	1.2	1.2	1.2	-	-	-	-	-	-
Water	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100
Emulsification index	3.9	4.0	4.0	3.9	3.8	3.7	2.8	2.5	2.8	2.8	2.6	2.7
Emulsification effect	good	good	good	good	good	good	moderate	moderate	moderate	moderate	moderate	moderate

[0087] The stability test shows that the uncrosslinked polymers according to the invention in combination with additional thickening agents give stable emulsions.

Test emulsions with crosslinked polymers according to the invention

[0088]

Composition	32	33	34	35	36	37	38	39	40
Polymer acc. to Ex. 3	1	1	1	1	1	1	0.75	0.75	0.75
Oil mixture I	27			27			27		
Oil mixture II		27			27			27	
Oil mixture III			27			27			27
Carbopol 980	0.3	0.3	0.3	-	-	-	-	-	-
Sodium hydroxide 10%	1.2	1.2	1.2	-	-	-	-	-	-
Water	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100	Ad 100
Emulsification index	4.7	4.8	4.7	4.6	4.4	4.5	4.5	4.6	4.6
Emulsification effect	very good	very good	very good	very good	very good	very good	very good	very good	very good

[0089] The stability test shows that the crosslinked polymers according to the invention act simultaneously as thickening agent and as emulsifier with very good emulsifier properties. Stable emulsions are obtained without additional co-emulsifiers and without additional thickening agents.

[0090] Examples of formulations, all data in wt. %.

Example 41: O/W - Skin Milk<sup>3</sup>

Composition:

[0091]

A	®Polymer acc. to Ex. 2	0.50%
	Mineral oil, low viscos.	6.00%
	®Miglyol 812 (Dynamit Nobel)	4.00%
	Capryl/caprin triglyceride	
	Isopropyl palmitate	6.00%
	Soybean oil	3.00%
B	Jojoba oil	2.00%
	®Aristoflex AVC (Clariant)	30%
	AMPS/VIFA copolymer	
C	®Hostapon KCG (Clariant)	1.00%
	Sodium cocoyl glutamate	
	Water	ad 100%
D	Glycerin	3.00%
	Sodium hydroxide (10% in water)	1.20%
	Fragrances	0.30%

Production

[0092]

- I Stir B into A, add C and mix in well
- II Stir D into I
- III Homogenize emulsion

---

<sup>3</sup> or skin lotion

Example 42: O/W - Skin Milk

Composition:

[0093]

A	®Polymer acc. to Ex. 1	0.50%
	Isopropyl palmitate	4.00%
	Almond oil	4.00%
	Wheat germ oil	1.00%
	®Cetion SN (Henkel)	8.00%
	Cetearyl <sup>4</sup> isononanoate	
B	®Aristoflex AVC (Clariant)	0.30%
	AMPS/VIFA copolymer	
C	Water	ad 100%
D	Fragrances	0.30%

Production

[0094]

- I Mix A and B, then add C
- II Add D to I
- III Homogenize emulsion

---

<sup>4</sup> Typographic error in the original

Example 43: O/W - After-Sun-Milk

Composition:

[0095]

A	®Polymer acc. to Ex. 1	1.00%
	Isopropyl palmitate	5.00%
	®Cetion SN (Henkel)	4.00%
	Cetearyl isononanoate	
	Soybean oil	4.00%
	®Miglyol 812 (Dynamit Nobel)	3.00%
	Capryl/caprin triglyceride	
	Jobba oil	3.00%
	Wheat germ oil	1.00%
	®AQUAMOLLIN BC powder highly conc. (Clariant)	0.10%
D	Ethylene diamine tetraacetic acid sodium salt	
	Citric acid (10%)	0.30%
	Water	68.80%
	Glycerin	3.00%
	ALLANTOIN (Clariant)	0.20%
C	Preservative	q.s
	Ethanol	1.50%
	Perfume oil	0.30%

Production

[0096]

- I Homogeneously stir together the components of A
- II Stir D into I at approx. 35°C
- III Homogenize the emulsion

## Examples of water in oil formulations

Example 44: Reaction according to the general polymerization specification

[0097]

Reactant	Amount (g)
Genapol® T-250-methacrylate	90
NH <sub>3</sub> neutralized AMPS	10
TMPTA	1.5
t-butanol	300
Dilauroyl peroxide (initiator)	1

Examples 45: W/O - Cream

## Composition

[0098]

A	®HOSTACERIN DGI (Clariant)	4.00%
	Polyglyceryl-2-sesquiisostearate	
	Beeswax	2.00%
	Polymer acc. Ex. 18	1.5%
	Mineral oil, low viscosity	5.00%
	Vaseline	10.00%
	®Cetiol V (Henkel KGaA)	5.00%
B	Decyl Oleate	
	1,2-propylene glycol	3.00%
	Water	69.10%
C	Preservative	q.s
	Fragrance	0.40%

## Production

[0099]

- I Melt A at 80°C
- II Heat B to 80°C
- III Stir II into I
- IV Stir until cool
- V At 35°C add C to IV

## Examples of Surfactant Formulations

### Example 46: Body wash

#### Composition

##### [0100]

A	®GENAPOL LRO liquid (Clariant) Sodium laureth sulfate	40.00%
B	Fragrance	0.30%
C	Water	52.70%
	Dyestuff	q.s.
	Preservative	q.s.
	®FENAGEN LDA (Clariant)	6.00%
	Disodium lauroamphodiacetate	
	Citric acid	q.s.
D	Polymer acc. to Ex. 6	1.00%

#### Production

##### [0101]

- I Stir B into A
- II Add the components of C one after another to I
- III Adjust pH to 5.5
- IV Adjustment of the viscosity by stir ring D into II

Example 47: Body shampoo

Composition

[0102]

A	Water	60.70%
	®GENAPOL LRO liquid (Clariant)	25.00%
	Sodium laureth sulfate	
	®HOSTAPON GLC (Clariant)	8.00%
	Sodium sauroyl glutamate	
	®GENAPOL SBE (Clariant)	
	Disodium laureth sulfosuccinate	
	Fragrance	0.30%
	Dyestuff solution	q.s.
	Preservative	q.s.
B	Polymer acc. to Ex. 4	1.00%

Production

[0103]

- I Dissolve B in A
- II Possibly adjust pH

Example 48: Anti-dandruff shampoo, clear

Composition

[0104]

A	®OCTOPIROX (Clariant)	0.50%
	Piroctone olamine	25.00%
B	Water	10.00%
C	®GENAPOL LRO LIQUID (Clariant)	30.00%
	Sodium laureth sulfate	
D	®Belsil DMC 6032 (Wacker Chemie)	1.50%
	Dimethicone copolyol acetate	
	Fragrance	0.30%
E	®ALLANTOIN (Clariant)	0.30%
F	Water	46.40%
G	Dyestuff solution	q.s.
	Penthanol (Hoffmann La Roche)	1.00%
	®GENAGEN GAB (Clariant)	8.00%
	Cocamidopropyl betaine	
H	Polymer acc. to Ex. 7	1.10%

Production

[0105]

- I Mix A with B
- II Stir C into I until clear solution [forms]
- III Add components of D one after another to I
- IV Stir E into F under heating and then stir into I
- V Add components of G one after another to I
- VI Possibly adjust pH
- VII Adjustment of the viscosity by stirring H into I

Example 49: Anti-dandruff shampoo, pearlescent

Composition

[0106]

A	Water	38.7%
B	®HOSTAPON SCI-65 (Clariant)	3.00%
	Sodium cocoyl isethionate	10.00%
C	®GENAPOL LRO liquid (Clariant)	35.00%
	Sodium laureth sulfate	
	®HOSTAPON KCG (Clariant)	5.00%
	Sodium cocoyl glutamate	
	®Belsil DMC 6032 (Wacker)	1.00%
	Dimethicone copolyol acetate	
	Fragrance	0.30%
	®GENAGEN GAB (Clariant)	9.00%
	®Cocamidopropyl betaine	
	®GENAPOL TSM (Clariant)	4.00%
	PEG-3 distearate (and) sodium laureth Sulfate	
	Merquat 550	0.50%
	Polyquaternium-7	
	Zinc Omadine FPS (Olin)	
	Zinc Pyrithione (48%)	2.50%
	Polymer acc. to Ex. 9.1	1.00%
	Dyestuff solution	q.s.
	Preservatives	q.s.

Production

[0107]

- I Dissolve B in A at 80°C
- II Following cooling to approx. 35°C, add the components of C one after another

## Examples of Gels

### Example 50: Hair gel with conditioning properties

#### Composition

[0108]

A	Water	92.00%
	Panthenol	1.50%
	UVA-sorb 50	0.05%
	Benzophenone-4	
	Dyestuff solution	q.s.
B	Preservatives	q.s.
	®Emulsogen HCO 040 (Clariant)	0.50%
	PEG-40 hydrogenated castor oil	
	Perfumes	q.s.
C	Polymer according to Example 3	2.50%

#### Production

[0111]

- I Mix A components
- II Add B components
- III Add C to D to I

### Example 51: Hair gel with strong hold

#### Composition

[0110]

A	Water	91.50%
	PVP K-30 (ISP)	4.00%
	PVP	
	Panthenol	0.50%
	UVAsorb S5	0.05%
	Benzophenone-4	
	Dyestuff solution	q.s.
	Preservatives	q.s.
B	Abil B 8851 (Goldschmidt)	1.00%
	Dimethicone copolyol	
	®Emulsogen HCO 040 (Clariant)	0.50%
	PEG-40 hydrogenated castor oil	
	Perfumes	q.s.
C	Polymer according to Example 3	2.00%
D	Gafquat 755N (ISP)	2.50%
	Polyquaternium-11	

#### Production

[0111]

- I Mix components A
- II Add components B into I
- III Add components C into I

#### Patent Claims

##### 1. Water-soluble polymers, producible through the free -radical copolymerization a

A) one or more macromonomers, comprising an end group capable of polymerization, an hydrophilic part which is based on polyalkylene oxides, and a hydrophobic part which comprises hydrogen or a saturated or unsaturated, linear or branched, aliphatic, cycloaliphatic or aromatic (C<sub>1</sub>-C<sub>30</sub>) hydrocarbon residue, and

- B) one or more olefinically unsaturated comonomers which comprise oxygen, nitrogen, sulfur, phosphorus, chlorine and or fluorine.
2. Polymers according to claim 1, characterized in that in the case of the macromonomer A) one deals with those with the Formula (1)



where  $R^1$  represents a vinyl, allyl, acrylic or methacrylic residue;  $R^2$  ( $C_2-C_4$ ) alkylene; x an integer number between 1 and 500;  $Y = O, S, PH$  or  $NH$ ; and  $R^3$  hydrogen or a saturated or unsaturated linear or branched aliphatic, cycloaliphatic or aromatic ( $C_1-C_{30}$ ) hydrocarbon.

3. Polymer according to claim 1 and/or 2, characterized in that in the case of the comonomers B) one deals with olefinic unsaturated acids and/or their salts with mono- or divalent counterions, especially preferred acrylamidopropyl methylene sulfonic acid (AMPS); esters of the acrylic and the (meth)acrylic acid with aliphatic, aromatic or cycloaliphatic alcohols with a number of carbons of 1 to 22; esters of the acrylic and the (meth)acrylic acid with alkyl ethoxylates, open-chain and cyclic N-vinyl amides with a ring size of 4 to 9 atoms; amides of the acrylic and the methacrylic acid; 2-vinylpyridine; 4-vinylpyridine; vinyl acetate; glycidyl (meth)acrylate; acrylonitrile; vinyl chloride; vinylidene chloride; tetrafluoroethylene and/or DADMAC.
4. Polymers according to at least one of the claims 1 through 3, producible through the free-radical copolymerization of
- A) one or more macromonomers, selected from the group of the esters of the (meth)acrylic acid with alkylethoxylates, which comprise 5 to 80 EO units and ( $C_{10}-C_{22}$ ) alkyl residues, and
- B) one or more olefinically unsaturated comonomers, selected from the group of acrylamidopropyl methylene sulfonic acid (AMPS), sodium and ammonium salts of the acrylamidopropyl methylene sulfonic acid (AMPS), acrylamide, N-vinyl formamide, N-vinyl methyl acetamide and/or sodium methallyl sulfonate.

5. Polymers according to at least one of the claims 1 through 4, characterized in that the fraction of macromonomers is 50.1 -99.9 mol%.
6. Polymers according to at least one of the claims 1 through 4, characterized in that the fraction of macromonomers is 0.1 -50 mol%.
7. Polymers according to at least one of the claims 1 through 6, characterized in that they are crosslinked through the copolymerization of at least one crosslinking agent with at least two unsaturated double bonds.
8. Polymers according to at least one of the claims 1 through 6, characterized in that they consist of a water-soluble polymer backbone and macromonomers A) with thermally sensitive side chains, which in water have an LCST behavior, and the aqueous solution of which has a viscosity which above a certain threshold temperature increases or remains approximately constant with the increasing temperature.
9. Polymers according to at least one of the claims 1 through 7, characterized in that their aqueous solution has a viscosity which below a first threshold temperature is low, above this first line increases to a maximum with the increasing temperature, and decreases again with temperature above a threshold temperature.
10. Polymers according to at least one of the claims 1 through 7, characterized in that their 1% aqueous solutions exhibit at room temperature a viscosity of 20,000 mPas to 100,000 mPas and the solutions show no thermo -associating behavior.
11. Polymers according to at least one of the claims 1 through 10, characterized in that they are produced through precipitation polymerization in tert. -butanol.
12. Aqueous formulations, aqueous-alcoholic formulations, aqueous-surfactant formulations, emulsions and suspensions, comprising polymers according to at least one of the claims 1 through 11.
13. Formulations, emulsions and suspensions according to claim 12, characterized in that one deals thereby with cosmetics and pharmaceuticals.

14. Formulations, emulsions and suspensions according to claim 12 or 13, characterized in that in relation to the finished formulation, they comprise 0.05 to 10 wt.% of polymers.
15. Utilization of polymers according to at least one of the claims 1 through 11 as thickeners, dispersing agents, suspending agents, emulsifiers, stabilizers and/or thickening agents.
16. Utilization of polymers according to at least one of the claims 1 through 11 as adjuvants in crop protection chemicals.

# EUROPEAN RESEARCH REPORT

European Patent Office

Application Number  
EP 00 11 4625

EP 00 11 462

RELEVANT DOCUMENTS			
Category	Characteristics of the document with declaration, as required, of the pertinent parts	Related Claims	Classification of the Application (Int. Cl.7)
X	US 5 837 789 A (HARTAN HANS-GEORG ET AL) November 17, 1998 (1998-11-17) * Column 5, Line 28 - Column 7, Line 16 * ---	1-7	C08F290/06 A61K47/32 A61K7/48 A01N25/10
X	US 5 712 359 A (AUSCHRA CLEMENS ET AL) January 27, 1998 (1998-01-27) * Column 2, Line 20-64 * ---	1-4, 6	
X	WO 97 14448 A (LUTHRA AJAY KUMAR; SANDHU SHIVPAL SINGH (GB)) April 24, 1997 (1997-04-24) * Claim 1 * ---	1-3	
X	WO 94 24202 A (DOW CHEMICAL CO.; HELMER BRADLEY J (US); LOUGHNEY SHIRLEY J (US); M) October 27, 1994 (1994-10-27) * Claim 1 * ---	1-3	
X	US 5 395 907 A (ZAJACZKOWSKI MICHAEL J) March 7, 1995 (1995-03-07) * Column 3, Line 16 - Column 5, Line 34 * ---	1-3	Research Subject Area (Int. Cl.7)
X	US 5 480 953 A (SUGAYA HIROYUKI ET AL) January 2, 1996 (1996-01-02) * Claim 1 * ---	1-3	C08F A61K A01N
X	US 5 045 619 A (KURODA NOBUYUKI ET AL) September 3, 1991 (1991-09-03) * Column 3, Line 32-38 * ---	1-4	
X	US 5 086 142 A (FOCK JUERGEN ET AL) February 4, 1992 (1992-02-04) * Claims * ---	1-3, 12-16	
-/-			
The research report under consideration was performed for all patent claims			
Research location DEN HAAG		Date of completion of the research November 23, 2000	Examiner Meulemans, R.

## CATEGORIES OF THE NAMED DOCUMENTS:

- X: of special importance in itself
- Y: of special importance in relation to another publication in the same category
- A: technological background
- O: non-written revelation
- P: intermediate literature
- T: theories or principles on which the invention is based
- E: older patent document, that however was published simultaneously with or after the application date.
- D: document quoted in the application
- L: document quoted elsewhere

&: member of the same patent family, corresponding document

# EUROPEAN RESEARCH REPORT

European Patent Office

Application Number  
EP 00 11 4625

RELEVANT DOCUMENTS			
Category	Characteristics of the document with declaration, as required, of the pertinent parts	Related Claims	Classification of the Application (Int. Cl.7)
X	EP 0 850 894 A (NIPPON CATALYTIC CHEM IND) July 1, 1998 (1998-07-01) * Claim 1 *	1-6, 15	
X	GB 1 167 524 A (ICI) October 15, 1969 (1969-10-15) * Claim 1 *	1-6	
X	US 5 849 840 A (OHNISHI KIZO ET AL) December 15, 1998 (1998-12-15) * Claim 1 *	1-3, 5, 12	
The research report under consideration was performed for all patent claims			Research Subject Area (Int. Cl.7)
Research location DEN HAAG		Date of completion of the research November 23, 2000	Examiner Meulemans, R.
CATEGORIES OF THE NAMED DOCUMENTS:			
<p>X: of special importance in itself  Y: of special importance in relation to another publication in the same category  A: technological background  O: non-written revelation  P: intermediate literature  T: theories or principles on which the invention is based  E: older patent document, that however was published simultaneously with or after the application date.  D: document quoted in the application  L: document quoted elsewhere</p>			
&: member of the same patent family, corresponding document			

**APPENDIX TO THE EUROPEAN RESEARCH REPORT  
ABOUT THE EUROPEAN PATENT APPLICATION NO.**

EP 00 11 4625

Listed in this appendix are the members of the families of patents of the patent documents listed in the above mentioned European research report.

The statements about the family members correspond to the status of the file of the European patent office on

These statements serve in informing only and are made, no responsibility taken.

Nov. 23, 2000

Patent documents listed in the research report		Date of publication	Member(s) of the family of patents	Date of publication
US 5837789	A	17-11-1998	DE 19646484 A	22-05-1997
			AT 183526 T	15-09-1999
			AU 718132 B	06-04-2000
			AU 7627396 A	11-06-1997
			BR 9611469 A	15-06-1999
			CA 2236504 A	29-05-1997
			CN 1207745 A	10-02-1999
			DE 59602822 D	23-09-1999
			WO 9719116 A	29-05-1997
			EP 0862590 A	09-09-1998
			ES 2138385 T	01-01-2000
			PL 326840 A	26-10-1998
US 5712359	A	27-01-1998	DE 4423358 A	11-01-1996
			AT 179188 T	15-05-1999
			DE 59505684 D	27-05-1999
			EP 0691355 A	10-01-1996
			JP 8048727 A	20-02-1996
WO 9714448	A	24-04-1997	AU 704646 B	29-04-1999
			AU 7313696 A	07-05-1997
			EP 0964708 A	22-12-1999
			JP 11515050 T	21-12-1999
WO 9424202	A	27-10-1994	AU 4032393 A	08-11-1994
			US 5491209 A	13-02-1996
US 5395907	A	07-03-1995	AT 176796 T	15-03-1999
			AU 1330895 A	13-06-1995
			CA 2154483 A	01-06-1995
			DE 69416582 D	25-03-1999
			DE 69416582 T	02-09-1999
			EP 0681601 A	15-11-1995
			ES 2128037 T	01-05-1999
			WO 9514746 A	01-06-1995
			US 5508367 A	16-04-1996
			US 5565268 A	15-10-1996
			US 5726250 A	10-03-1998
			US 5731387 A	24-03-1998
US 5480953	A	02-01-1996	AT 188714 T	15-01-2000
			DE 69327578 D	17-02-2000
			DE 69327578 T	24-08-2000
			EP 0614923 A	14-09-1994
			ES 2140468 T	01-03-2000
			GR 3032681 T	30-06-2000

For more details about this appendix: see the official gazette of the European Patent Office, no. 12/82

**APPENDIX TO THE EUROPEAN RESEARCH REPORT  
ABOUT THE EUROPEAN PATENT APPLICATION NO.**

EP 00 11 4625

Listed in this appendix are the members of the families of patents of the patent documents listed in the above mentioned European research report.

The statements about the family members correspond to the status of the file of the European patent office on

These statements serve in informing only and are made, no responsibility taken.

Nov. 23, 2000

Patent documents listed in the research report		Date of publication	Member(s) of the family of patents	Date of publication
US 5480953	A		WO 9407931 A	14-04-1994
US 5045619	A	03-09-1991	JP 2035520 C	28-03-1996
			JP 7055926 B	14-06-1995
			JP 63238053 A	04-10-1988
			CA 1313882 A	23-02-1993
			FR 2612923 A	30-09-1988
			GB 2202848 A, B	05-10-1988
US 5086142	A	04-02-1992	DE 3925220 C	03-01-1991
			DE 59001428 D	17-06-1993
			EP 0413953 A	27-02-1991
			JP 1927266 C	25-04-1995
			JP 3074417 A	29-03-1991
			JP 6055801 B	27-07-1994
EP 0850894	A	01-07-1998	BR 9706470 A	08-06-1999
			JP 10236857 A	08-09-1998
			US 5912284 A	15-06-1999
			JP 10236858 A	08-09-1998
GB 1167524	A	15-10-1969	BE 705714 A	26-04-1968
			DE 1745006 A	30-03-1972
			FR 1541974 A	
			NL 6714411 A	29-04-1968
US 5849840	A	15-12-1998	KEINE	

For more details about this appendix: see the official gazette of the European Patent Office, no. 12/82